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(71) Applicant: KAO CORP

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(72) Inventor: SAWADA HIROKI  
ISHII YASUO

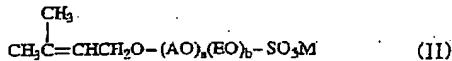
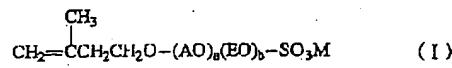
**(54) SURFACTANT COMPOSITION FOR EMULSION  
POLYMERIZATION**

## (57) Abstract:

**PROBLEM TO BE SOLVED:** To obtain a surfactant composition for an emulsion polymerization, providing a polymer emulsion having excellent stability during a polymerization and excellent physical properties of a coating film prepared from the formed polymer emulsion.

**SOLUTION:** This surfactant composition for emulsion polymerization comprises at least one kind selected from sulfuric ester salts of formula (I) or formula (II). The method for producing the polymer emulsion comprises carrying out an emulsion polymerization by using the surfactant composition.

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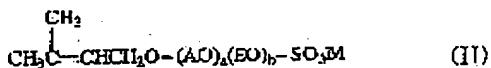
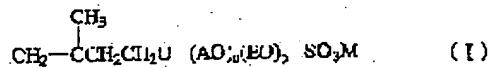
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### LEGAL STATUS

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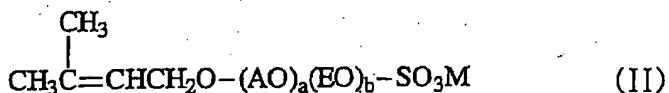
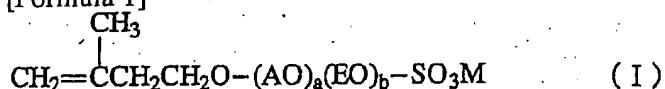
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**CLAIMS**

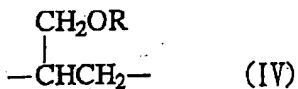
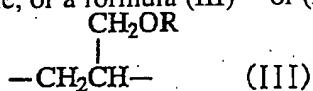
[Claim(s)]

[Claim 1] The surfactant constituent for emulsion polymerizations containing at least one sort chosen from the sulfate salt expressed with a formula (I) or (II).

[Formula 1]



the inside of [formula, and A -- the straight chain of carbon numbers 3-18, a branched chain alkylene machine, or a formula (III) -- or (IV) -- [Formula 2]



[-- R shows the straight chain or branched chain alkyl group of carbon numbers 4-18 among a formula As for 0-50b, the alkoxy methyl-ethylene machine expressed with) and EO show an oxyethylene machine, a shows the number of 0-200, and a and b are not simultaneously set to 0. M shows a cation. In addition, a pieces Block combination or random combination is sufficient as a -(AO)-machine and b -(EO)-machines, and, in block combination, any are sufficient as the array sequence of a -(AO)-machine and a -(EO)-machine. Moreover, a pieces Even if a -(AO)-machine is the same, they may differ.]

[Claim 2] The manufacturing method of the polymer emulsion which performs an emulsion polymerization using a surfactant constituent according to claim 1.

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacturing method of the surfactant constituent for emulsion polymerizations, and the polymer emulsion which uses this.

[0002]

[Description of the Prior Art] Fields, such as a paint, adhesives, paper processing, and textile finishing, or a polymer is separated as it is, and the polymer emulsion obtained according to the emulsion polymerization of vinyl system monomers, such as vinyl acetate and an acrylic ester, is widely used industrially as plastics and rubber. Nonionic surface active agents, such as anionic surfactants, such as an alkyl-sulfuric-acid ester salt, alkylbenzene sulfonates, a polyoxyethylene-alkyl-ether salt, and a polyoxyethylene-alkyl-phenyl-ether salt, and polyoxyethylene alkyl ether, and polyoxyethylene alkyl phenyl ether, are used for the emulsion polymerization as an emulsifier.

[0003] The emulsifier in an emulsion polymerization influences the stability of the polymer emulsion under polymerization, the mechanical stability of the polymer emulsion generated further, chemical stability, freeze thaw stability, and storage stability, and further, emulsion physical properties, such as a particle diameter of a polymer emulsion, viscosity, and foarnability, and when it film-izes further, it not only affects the initiation reaction of a polymerization, and propagation, but has big influence on film physical properties, such as the water resistance, moisture resistance, thermal resistance, an adhesive property, and adhesiveness. Although a polymer paint film is formed by dryness of a polymer emulsion, the cause and bird clapper to which the emulsifier which remains into a polymer paint film reduces water resistance, an adhesive property, weatherability, thermal resistance, etc. are known for the use of a paint, adhesives, etc. Moreover, in manufacture of synthetic rubber etc., in case polymer is taken out from a polymer emulsion with meansas, such as a salting-out, while draining, an emulsifier is contained, and there is a problem that the burden of waste water treatment becomes large.

[0004] In order to solve such a fault, the method using the so-called reactive surface active agent of having the unsaturated bond of ethylene nature as a polymerization nature machine in a molecule is proposed. For example, in JP,61-223011,A, the method using the ethereal-sulfate ester salt of the polyoxyalkylene which had an allyl compound or a metallyl machine as a polymerization nature machine is indicated. Moreover, the result which performed the emulsion polymerization to Macromolecules, 32 volumes, and 5967 pages (1999) using the oxy-alkane sulfonic-acid sodium and 10-(3-methyl-3-BUTENIRUOKISHI) Deccan-1-sulfonic-acid sodium which use a 3-methyl-3-but enyl group as a polymerization nature machine is indicated.

[0005] However, when these reactive surface active agents are independently used as an emulsifier for emulsion polymerizations, there is a problem that it is common for the stability at the time of a polymerization to be inadequate, and it must use the emulsifier of a conventional type together in that case. Moreover, in the case of 10-(3-methyl-3-BUTENIRUOKISHI) Deccan-1-sulfonic-acid sodium, there is a problem that the own manufacture of the very thing is not easy from fields, such as reaction temperature and yield, and is inferior to economical efficiency.

[0006] The technical problem of this invention has the stability of the polymer emulsion under polymerization, or the physical properties of the polymer paint film produced from the generated

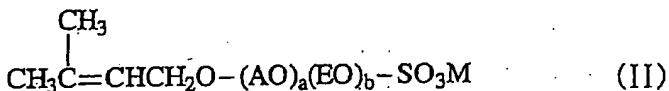
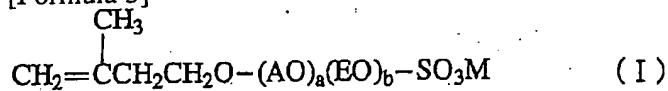
polymer emulsion in offering the manufacturing method of the surfactant constituent for emulsion polymerizations which gives a good polymer emulsion, and the polymer emulsion using this.

[0007]

[Means for Solving the Problem] this invention is the manufacturing method of the surfactant constituent for emulsion polymerizations containing at least one sort chosen from the sulfate salt expressed with a formula (I) or (II), and the polymer emulsion which performs an emulsion polymerization using this surfactant constituent.

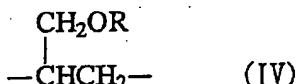
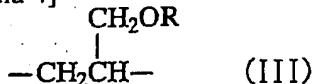
[0008]

[Formula 3]



[0009] the inside of [formula, and A -- the straight chain of carbon numbers 3-18, a branched chain alkylene machine, or a formula (III) -- or (IV) -- [0010]

[Formula 4]



[0011] (R shows the straight chain or branched chain alkyl group of carbon numbers 4-18 among a formula As for 0-50b, the alkoxy methyl-ethylene machine expressed with) and EO show an oxyethylene machine, a shows the number of 0-200, and a and b are not simultaneously set to 0. M shows a cation. In addition, a pieces Block combination or random combination is sufficient as a -(AO)-machine and b -(EO)-machines, and, in block combination, any are sufficient as the array sequence of a -(AO)-machine and a -(EO)-machine. Moreover, a pieces Even if a -(AO)-machine is the same, they may differ.]

[0012]

[Embodiments of the Invention] In the aforementioned formula (I) or (II), a propylene, ethyl ethylene, dimethyl ethylene, butyl ethylene, octyl ethylene, a decylethylene, dodecyl ethylene, tetradecyl ethylene, hexadecyl ethylene, etc. are mentioned as the straight chain or branched chain alkylene machine of carbon numbers 3-18 shown by A. As the straight chain or branched chain alkyl group of carbon numbers 4-18 shown by R in a formula (III) or (IV), a butyl, a pentyl machine, a hexyl machine, an octyl machine, a 2-ethylhexyl machine, a nonyl machine, a decyl group, a undecyl machine, a dodecyl machine, a tetradecyl machine, a hexadecyl machine, an octadecyl machine, etc. are mentioned. a shows the number of average addition mols of an oxy-alkylene machine or an alkoxy methoxy ethylene, and 0-50, and when it is in the range of 0-20 preferably and does not use other surfactants together, the carbon number of A or R and a have especially the desirable number with which are satisfied of a formula (V).

[0013]

$5 \leq (\text{carbon number } -2.8 \text{ of A or R}) \times a \leq 15$  (V)  
 b -- the number of average addition mols of an oxyethylene machine -- being shown -- 0-200 -- although it is in the range of 1-50 preferably, a and b are not simultaneously set to 0 Chemical stability will become inadequate if a and b are simultaneously set to 0. Moreover, a pieces Block combination or random combination is sufficient as a -(AO)-machine and b -(EO)-machines, and, in block combination, any are sufficient as the array sequence of a -(AO)-machine and a -(EO)-

machine. Moreover, even if a piece of a -(AO)-machine is the same, they may differ. As a cation shown by M, alkaline-earth-metal ion, such as alkali-metal ion, such as sodium and a potassium, calcium, and magnesium, an ammonium ion, the ammonium ion replaced by the alkyl group of carbon numbers 1-4 are mentioned.

[0014] The sulfate salt (I) concerning this invention or (II) It can manufacture using a well-known method. to 3-methyl-3-butene-1-oar Under catalyst existence, Alpha olefin epoxide or alkyl glycidyl ether is added. [ whether an ethyleneoxide is added to the obtained resultant according to a conventional method, and ] Or after adding an ethyleneoxide to 3-methyl-3-butene-1-oar, It carries out whether alpha olefin epoxide or alkyl glycidyl ether is added, and ether alcohol is obtained, and this is sulfurated by the sulfating agent and it is obtained by neutralizing by the alkali. Since the ammonium salt is already formed as a sulfating agent when an amidosulfuric acid is used although a chlorosulfonic acid, sulfuric anhydride, and an amidosulfuric acid are mentioned, the neutralization by the alkali is not necessarily required.

[0015] Although the surfactant constituent of this invention contains at least one sort of a sulfate salt (I) or (II), it is desirable to contain a sulfate salt (I) from the physical-properties side of the polymer paint film produced from the generated polymer emulsion.

[0016] Although other anionic surfactants or nonionic surface active agents can also be used together in the surfactant constituent of this invention, a sulfate salt (I) or the sum total content of (II) has 5 - 100 desirable % of the weight, and its 20 - 100 % of the weight is more desirable.

[0017] The manufacturing method of the polymer emulsion of this invention is the method of carrying out the emulsion polymerization of the vinyl system monomer using the surfactant constituent concerning this invention. In an emulsion polymerization, the amount of the surfactant constituent used has 0.1 - 10 desirable % of the weight to the total amount of a vinyl system monomer.

[0018] As a vinyl system monomer used by this invention Aromatic vinyl monomers, such as styrene, an alpha methyl styrene, and chloro styrene; (meta) A methyl acrylate, Acrylic-ester (meta); (meta) acrylic acids, such as butyl-acrylate and acrylic-acid (meta) 2-ethylhexyl; A vinyl chloride, (Meta) A halogenation vinyl and halogenation vinylidenes, such as vinyl bromide and a vinylidene chloride; Vinyl acetate, vinyl-esters [, such as a propionic-acid vinyl, ]; (meta) -- nitril [, such as acrylonitrile ]; -- conjugated dienes, such as a butadiene and an isoprene, are mentioned, and even if it carries out the polymerization of these monomers independently, they may carry out copolymerization of the two or more sorts The amount of the vinyl system monomer used has 40 - 60 desirable % of the weight to the whole system.

[0019] As an initiator used for the emulsion polymerization of this invention, although azo system compounds, such as organic peroxide [, such as inorganic peroxides, such as potassium persulfate, an ammonium persulfate, and a hydrogen peroxide, t-butyl peroxide cumene hydroxy peroxide, and PARAMEN tamper oxide, ], azobis diisobutyl nitril, 2, and 2'-azobis (2-amidinopropane) dihydrochloride, are mentioned for example, persulfates, such as potassium persulfate and an ammonium persulfate, are desirable. Moreover, a sodium hydrogensulfite, an ammonium ferrous sulfate, etc. can also be used as a polymerization promotor.

[0020] Although the addition method of a monomer can use a monomer dropping test, a monomer package preparation method, or the pre emulsion method, polymerization stability to its pre emulsion method is desirable. 1 - 5 hours of a maturing time are [ a drop time ] desirable for 1 to 8 hours. Although polymerization temperature is adjusted by the decomposition temperature of an initiator, in the case of a persulfate, 70-80 degrees C is desirable.

[0021]

[Example] % in an example is weight % unless it mentions specially.

[0022] It blended at a rate which shows the anionic surfactant of the sulfate salt concerning this invention manufactured by the method shown in examples 1-12 and the example 1 of comparison - 3 following, and a conventional type in Table 1, and this invention and the comparative surfactant constituent were prepared. The emulsion polymerization was performed by the method shown below using this surfactant constituent, and the method shown below estimated the performance. A result is shown in Table 1.

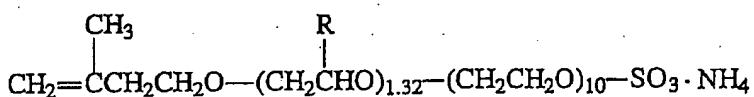
[0023] <Example of manufacture of sulfate salt> sulfate salt [A-1] agitator, a thermometer, a tap

funnel, and reflux pipe. 3-methyl-3-butene-1-all (made in Tokyo Chemicals) 397g (4.6 mols) and powder sodium METOKI side 3.11g (0.0576 mols) were taught to the reaction container which it had, alpha-olefin epoxide (AOE X24, Daicel Chemical Industries, Ltd. make) 236.7g (1.15 mols) of carbon numbers 12 and 14 was dropped over 4 hours at 130 degrees C under nitrogen-gas-atmosphere mind, and it riped at this temperature for 12 hours. The reflux pipe was changed to the distilling tube and unreacted 3-methyl-3-butene-1-oar was removed under reduced pressure.

According to 1 H-NMR, the number of average addition mols of alpha-olefin epoxide was 1.32. 300g of obtained reaction mixture was taught to the autoclave, and ethyleneoxide 477g was added on condition that 140 degrees C and 0.3MPa. Next, sulfate salt which teaches 87.8g of a part of obtained reaction mixture, and 12.0g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-1] was obtained.

[0024]

[Formula 5]

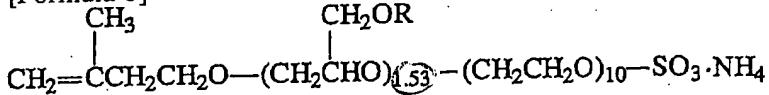


(R : n-C<sub>10</sub>H<sub>21</sub>基とn-C<sub>12</sub>H<sub>25</sub>基の混合物)

[0025] Sulfate salt 3-methyl-3-butene-1-all 310g (3.6 mols) and powder sodium METOKI side 1.95g (0.0361 mols) were taught to the reaction container equipped with [A-2] agitator, the thermometer, the tap funnel, and the reflux pipe, and it was dropped at 130 degrees C under nitrogen-gas-atmosphere mind, having 2-ethylhexyl glycidyl ether 223.6 bet it for 2 hours and a half (1.2 mols), and riped at this temperature for 5 hours. The reflux pipe was changed to the distilling tube and unreacted 3-methyl-3-butene-1-oar was removed under reduced pressure. According to 1 H-NMR, the number of average addition mols of 2-ethylhexyl glycidyl ether was 1.53. 284g of obtained reaction mixture was taught to the autoclave, and ethyleneoxide 438g was added on condition that 130 degrees C and 0.4MPa. Next, sulfate salt which teaches 88.4g of a part of obtained reaction mixture, and 12.6g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-2] was obtained.

[0026]

[Formula 6]

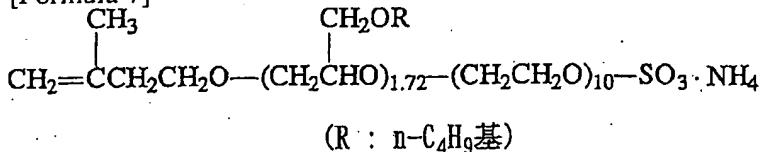


(R : 2-エチルヘキシル基)

[0027] Sulfate salt 3-methyl-3-butene-1-all 1801g (2.1 mols) and powder sodium METOKI side 3.40g (0.0629 mols) were taught to the reaction container equipped with [A-3] agitator, the thermometer, the tap funnel, and the reflux pipe, butyl-glycidyl-ether 273.4g (2.1 mols) was dropped over 2 hours at 140 degrees C under nitrogen-gas-atmosphere mind, and it riped at this temperature for 7 hours. The reflux pipe was changed to the distilling tube and unreacted 3-methyl-3-butene-1-oar was removed under reduced pressure. According to 1 H-NMR, the number of average addition mols of butyl glycidyl ether was 1.72. 368g of obtained reaction mixture was taught to the autoclave, and ethyleneoxide 558g was added on condition that 140 degrees C and 0.4MPa. Next, sulfate salt which teaches 82.9g of a part of obtained reaction mixture, and 11.4g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-3] was obtained.

[0028]

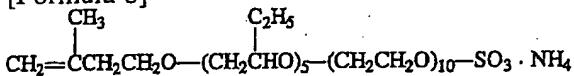
[Formula 7]



[0029] Sulfate salt 3-methyl-3-butene-1-all 390g (4.5 mols) and KOH7.58g (0.1351 mols) were taught to [A-4] autoclave, 1 and 2-epoxy butane 1621g (22.5 mols) was added on condition that 145 degrees C and 0.3MPa, and ethyleneoxide 1985g (45 mols) was continuously added on condition that 150 degrees C and 0.3MPa. Next, sulfate salt which teaches 261g of a part of obtained reaction mixture, and 34.7g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfuates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-4] was obtained.

[0030]

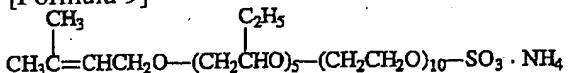
[Formula 8]



[0031] Sulfate salt 3-methyl-2-butene-1-all (made in Tokyo Chemicals) 310g (3.6 mols) and powder sodium METOKI side 7.26g (0.134 mols) were taught to [A-5] autoclave, 1 and 2-epoxy butane 1298g (18 mols) was added on condition that 130 degrees C and 0.3MPa, and ethyleneoxide 1586g (36 mols) was added continuously. Next, sulfate salt which teaches 84.7g of a part of obtained reaction mixture, and 9.60g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfuates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-5] was obtained.

[0032]

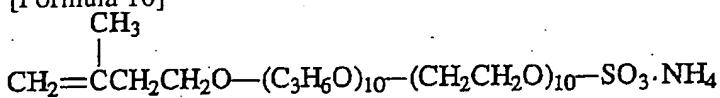
[Formula 9]



[0033] Sulfate salt 3-methyl-3-butene-1-all 301g (3.49 mols) and powder sodium METOKI side 11.3g (0.209 mols) were taught to [A-6] autoclave, propylene oxide 2030g (34.9 mols) was added on condition that 130 degrees C and 0.3MPa, and ethyleneoxide 1537g (34.9 mols) was added continuously. Next, sulfate salt which teaches 81.1g of a part of obtained reaction mixture, and 8.42g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfuates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-6] was obtained.

[0034]

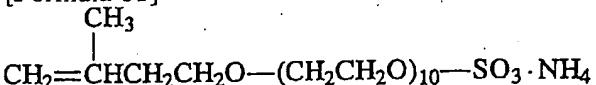
[Formula 10]



[0035] Sulfate salt 3-methyl-3-butene-1-all 340g (3.95 mols) and powder sodium METOKI side 6.40g (0.118 mols) were taught to [A-7] autoclave, and ethyleneoxide 1740g (39.5 mols) was added on condition that 130 degrees C and 0.3MPa. Next, sulfate salt which teaches 100g of a part of obtained reaction mixture, and 19.9g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfuates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-7] was obtained.

[0036]

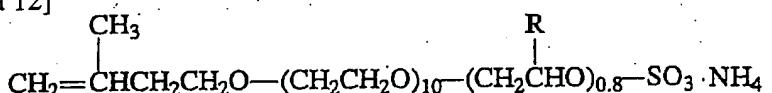
[Formula 11]



[0037] Sulfate salt It is a sulfate salt to the reaction container equipped with [A-8] agitator and the thermometer. 76.7g (0.15 mols) of ten mol adducts of ethyleneoxides of the 3-methyl-3-butene-1-oar obtained by the method shown in the example of manufacture of [A-7], Powder sodium METOKI side 0.243g (0.0045 mols) was taught, alpha-olefin epoxide (AOE X24, Daicel Chemical Industries, Ltd. make) 24.7g (0.12 mols) of carbon numbers 12 and 14 was dropped over 1 hour at 140 degrees C under nitrogen-gas-atmosphere mind, and it riped at this temperature for 4 hours. Next, sulfate salt which adds 14.18g of amidosulfuric acids, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-8] was obtained.

[0038]

[Formula 12]



(R : n-C<sub>10</sub>H<sub>21</sub>基とn-C<sub>12</sub>H<sub>25</sub>基の混合物)

[0039] 5.5g of surfactant constituents and 0.28g of potassium persulfate were dissolved in the <emulsion-polymerization method> beaker at 117.8g of \*\*\*\*\* ion exchange water, 2.8g of acrylic acids, 136.1g of butyl acrylates, and 136.1g of methyl methacrylates were added, it emulsified for 5000 r/minx 10 minutes in the homomixer, and the monomer emulsification object was obtained. 137.9g of ion exchange water, 0.25g of potassium persulfate, and the 36.2g of the above-mentioned monomer emulsification objects were taught to the separable flask, and it agitated for 15 minutes in the nitrogen air current. Next, agitating in a nitrogen air current, by the water bath, among flasks, the temperature up was carried out until it became 80 degrees C, the 326.4g of the above-mentioned monomer emulsification objects was dropped over 3 hours after the temperature up from the tap funnel, and after 1-hour digestion, \*\* cooled to the room temperature and obtained the polymer emulsion. The temperature between dropping and digestion and in a flask was kept at 80\*\*2 degrees C. Moreover, when the dropped monomer emulsification object dissociated within a tap funnel, the small agitator was inserted into the tap funnel and homogeneity was maintained.

[0040] The <performance-evaluation method> (1) polymerization stability polymer emulsion was filtered at the wire gauze made from stainless steel of 200 meshes, and the aggregates adhering to a reactor wall, an impeller, etc. after a polymerization were also collected, and it filtered similarly, it carried out 2-hour dryness and weighing capacity at 26.6kPa and 105 degrees C after rinsing, and the amount of aggregates was calculated. Polymerization stability was expressed with weight % of the aggregate to the total amount of the used monomer.

[0041] (2) Polymer emulsion 50g neutralized with 25% aqueous ammonia of mechanical stability was rotated for 5 minutes on condition that 10kgf(s) and 1000 r/min in the chestnut stable tester, the generated aggregate was filtered at the wire gauze made from stainless steel of 200 meshes, and after rinsing a filtration residue, it displayed at 26.6kPa(s) and 105 degrees C by dryness and weight [ as opposed to / carry out weighing capacity and / polymer ] %.

[0042] (3) Dynamic-light-scattering particle-size measuring device coal tar N4 Plus by the mean-particle-diameter Beckmann coal tar company was used, and the mean particle diameter of the polymer emulsion particle neutralized with aqueous ammonia 25% was measured.

[0043] (4) The viscosity Brookfield viscometer was used and the viscosity of the polymer emulsion neutralized with aqueous ammonia 25% was measured by the temperature of 25 degrees C, and rotational frequency 12 r/min.

[0044] (5) The polymer emulsion neutralized with aqueous ammonia 25% was applied on the waterproof slide glass board of a polymer film, it dried at 60 degrees C, and the polymer film was

produced. It was under 25-degree C ion exchange water, and the following criteria estimated the milkiness situation.

O after 1-hour progress -- completely -- after milkiness-less O: 1-hour progress -- a little -- milkiness

\*\*: 10 - 30 minutes -- milkiness x: -- immediately -- milkiness [0045]

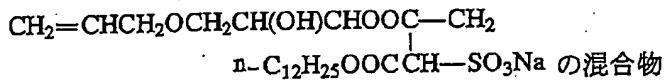
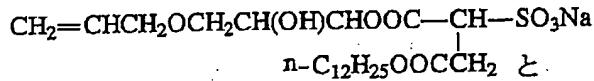
[Table 1]

		界面活性剤組成物(%)		重合 安定性 (%)	機械的 安定性 (%)	平均 粒径 (nm)	粘度 (mPa·s)	ポリマー フィルム の耐水性
		本発明に係わる 硫酸エステル塩	従来型陰イオン 界面活性剤 <sup>*1</sup>					
実 施 例	1	A-1 (100)		0.15	0.19	178	690	◎
	2	A-2 (100)		0.28	0.37	152	2060	◎
	3	A-3 (100)		0.23	0.01	408	37	○
	4	A-4 (100)		0.22	0.16	244	153	◎
	5	A-5 (100)		0.17	0.03	371	54	○
	6	A-6 (100)		0.10	0.01	469	38	○
	7	A-7 (100)		0.29	0.01	588	1.5	○
	8	A-8 (100)		0.26	0.01	306	9.3	◎
	9	A-6 (80) A-1 (20)		0.19	0.11	193	540	◎
	10	A-7 (80) A-1 (20)		0.17	0.01	281	100	◎
	11	A-6 (80)	B-1 (20)	0.16	0.09	200	453	○
	12	A-6 (20)	B-1 (80)	0.13	0.11	154	2350	○
比較 例	1		B-1 (100)	0.62	0.07	164	1518	○
	2		B-2 (100)	0.32	1.2	163	1200	×
	3		B-3 (100)	0.41	0.05	538	5.2	△

[0046] - 06. [Formula 13]

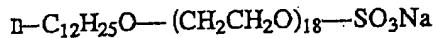
\*1 従来型陰イオン界面活性剤

B-1:

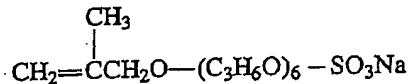


(特開昭 58-203960 号記載の方法で合成したもの)

B-2:



B-3:



(特開昭 61-223011 号記載の方法で合成したもの)

[0047]

[Effect of the Invention] If the surfactant constituent of this invention is used as an emulsifier for

emulsion polymerizations, polymerization stability and mechanical stability will be good and a polymer emulsion with the good water resistance when moreover making it a polymer film will be obtained.

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[Translation done.]

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TECHNICAL FIELD

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[The technical field to which invention belongs] this invention relates to the manufacturing method of the surfactant constituent for emulsion polymerizations, and the polymer emulsion which uses this.

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[Translation done.]

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**EFFECT OF THE INVENTION**

---

[Effect of the Invention] If the surfactant constituent of this invention is used as an emulsifier for emulsion polymerizations, polymerization stability and mechanical stability will be good and a polymer emulsion with the good water resistance when moreover making it a polymer film will be obtained.

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## TECHNICAL PROBLEM

[Description of the Prior Art] Fields, such as a paint, adhesives, paper processing, and textile finishing, or a polymer is separated as it is, and the polymer emulsion obtained according to the emulsion polymerization of vinyl system monomers, such as vinyl acetate and an acrylic ester, is widely used industrially as plastics and rubber. Nonionic surface active agents, such as anionic surfactants, such as an alkyl-sulfuric-acid ester salt, alkylbenzene sulfonates, a polyoxyethylene-alkyl-ether salt, and a polyoxyethylene-alkyl-phenyl-ether salt, and polyoxyethylene alkyl ether, and polyoxyethylene alkyl phenyl ether, are used for the emulsion polymerization as an emulsifier.

[0003] The emulsifier in an emulsion polymerization influences the stability of the polymer emulsion under polymerization, the mechanical stability of the polymer emulsion generated further, chemical stability, freeze thaw stability, and storage stability, and further, emulsion physical properties, such as a particle diameter of a polymer emulsion, viscosity, and foamability, and when it film-izes further, it not only affects the initiation reaction of a polymerization, and propagation, but has big influence on film physical properties, such as the water resistance, moisture resistance, thermal resistance, an adhesive property, and adhesiveness. Although a polymer paint film is formed by dryness of a polymer emulsion, the cause and bird clapper to which the emulsifier which remains into a polymer paint film reduces water resistance, an adhesive property, weatherability, thermal resistance, etc. are known for the use of a paint, adhesives, etc. Moreover, in manufacture of synthetic rubber etc., in case polymer is taken out from a polymer emulsion with meansas, such as a salting-out, while draining, an emulsifier is contained, and there is a problem that the burden of waste water treatment becomes large.

[0004] In order to solve such a fault, the method using the so-called reactive surface active agent of having the unsaturated bond of ethylene nature as a polymerization nature machine in a molecule is proposed. For example, in JP,61-223011,A, the method using the ethereal-sulfate ester salt of the polyoxyalkylene which had an allyl compound or a metallyl machine as a polymerization nature machine is indicated. Moreover, the result which performed the emulsion polymerization to Macromolecules, 32 volumes, and 5967 pages (1999) using the oxy-alkane sulfonic-acid sodium and 10-(3-methyl-3-BUTENIRUOKISHI) Deccan-1-sulfonic-acid sodium which use a 3-methyl-3-butetyl group as a polymerization nature machine is indicated.

[0005] However, when these reactive surface active agents are independently used as an emulsifier for emulsion polymerizations, there is a problem that it is common for the stability at the time of a polymerization to be inadequate, and it must use the emulsifier of a conventional type together in that case. Moreover, in the case of 10-(3-methyl-3-BUTENIRUOKISHI) Deccan-1-sulfonic-acid sodium, there is a problem that the own manufacture of the very thing is not easy from fields, such as reaction temperature and yield, and is inferior to economical efficiency.

[0006] The technical problem of this invention has the stability of the polymer emulsion under polymerization, or the physical properties of the polymer paint film produced from the generated polymer emulsion in offering the manufacturing method of the surfactant constituent for emulsion polymerizations which gives a good polymer emulsion, and the polymer emulsion using this.

[Translation done.]

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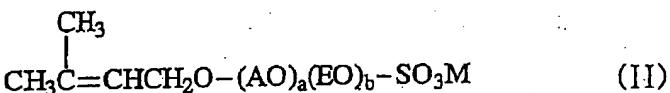
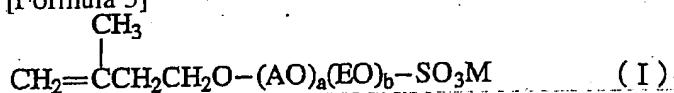
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## MEANS

[Means for Solving the Problem] this invention is the manufacturing method of the surfactant constituent for emulsion polymerizations containing at least one sort chosen from the sulfate salt expressed with a formula (I) or (II), and the polymer emulsion which performs an emulsion polymerization using this surfactant constituent.

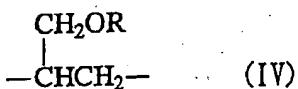
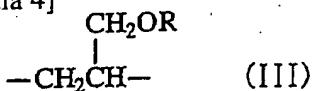
[0008]

[Formula 3]



[0009] the inside of [formula, and A -- the straight chain of carbon numbers 3-18, a branched chain alkylene machine, or a formula (III) -- or (IV) -- [0010]

[Formula 4]



[0011] (R shows the straight chain or branched chain alkyl group of carbon numbers 4-18 among a formula As for 0-50b, the alkoxy methyl-ethylene machine expressed with) and EO show an oxyethylene machine, a shows the number of 0-200, and a and b are not simultaneously set to 0. M shows a cation. In addition, a pieces Block combination or random combination is sufficient as a -(AO)-machine and b -(EO)-machines, and, in block combination, any are sufficient as the array sequence of a -(AO)-machine and a -(EO)-machine. Moreover, a pieces Even if a -(AO)-machine is the same, they may differ.]

[0012]

[Embodiments of the Invention] In the aforementioned formula (I) or (II), a propylene, ethyl ethylene, dimethyl ethylene, butyl ethylene, octyl ethylene, a decylethylene, dodecyl ethylene, tetradecyl ethylene, hexadecyl ethylene, etc. are mentioned as the straight chain or branched chain alkylene machine of carbon numbers 3-18 shown by A. As the straight chain or branched chain alkyl group of carbon numbers 4-18 shown by R in a formula (III) or (IV), a butyl, a pentyl machine, a hexyl machine, an octyl machine, a 2-ethylhexyl machine, a nonyl machine, a decyl group, a undecyl machine, a dodecyl machine, a tetradecyl machine, a hexadecyl machine, an octadecyl machine, etc. are mentioned. a shows the number of average addition mols of an oxy-alkylene machine or an alkoxy methoxy ethylene, and 0-50, and when it is in the range of 0-20 preferably and does not use

other surfactants together, the carbon number of A or R and a have especially the desirable number with which are satisfied of a formula (V).

[0013]

$5 \leq (\text{carbon number } - 2.8 \text{ of A or R}) \times a \leq 15$  (V)

b -- the number of average addition mols of an oxyethylene machine -- being shown -- 0-200 -- although it is in the range of 1-50 preferably, a and b are not simultaneously set to 0 Chemical stability will become inadequate if a and b are simultaneously set to 0. Moreover, a pieces Block combination or random combination is sufficient as a -(AO)-machine and b -(EO)-machines, and, in block combination, any are sufficient as the array sequence of a -(AO)-machine and a -(EO)-machine. Moreover, a pieces Even if a -(AO)-machine is the same, they may differ. As a cation shown by M, alkaline-earth-metal ion, such as alkali-metal ion, such as sodium and a potassium, calcium, and magnesium, an ammonium ion, the ammonium ion replaced by the alkyl group of carbon numbers 1-4 are mentioned.

[0014] The sulfate salt (I) concerning this invention or (II) It can manufacture using a well-known method. to 3-methyl-3-butene-1-oar Under catalyst existence, Alpha olefin epoxide or alkyl glycidyl ether is added. [ whether an ethyleneoxide is added to the obtained resultant according to a conventional method, and ] Or after adding an ethyleneoxide to 3-methyl-3-butene-1-oar, It carries out whether alpha olefin epoxide or alkyl glycidyl ether is added, and ether alcohol is obtained, and this is sulfurated by the sulfating agent and it is obtained by neutralizing by the alkali. Since the ammonium salt is already formed as a sulfating agent when an amidosulfuric acid is used although a chlorosulfonic acid, sulfuric anhydride, and an amidosulfuric acid are mentioned, the neutralization by the alkali is not necessarily required.

[0015] Although the surfactant constituent of this invention contains at least one sort of a sulfate salt (I) or (II), it is desirable to contain a sulfate salt (I) from the physical-properties side of the polymer paint film produced from the generated polymer emulsion.

[0016] Although other anionic surfactants or nonionic surface active agents can also be used together in the surfactant constituent of this invention, a sulfate salt (I) or the sum total content of (II) has 5 - 100 desirable % of the weight, and its 20 - 100 % of the weight is more desirable.

[0017] The manufacturing method of the polymer emulsion of this invention is the method of carrying out the emulsion polymerization of the vinyl system monomer using the surfactant constituent concerning this invention. In an emulsion polymerization, the amount of the surfactant constituent used has 0.1 - 10 desirable % of the weight to the total amount of a vinyl system monomer.

[0018] As a vinyl system monomer used by this invention Aromatic vinyl monomers, such as styrene, an alpha methyl styrene, and chloro styrene; (meta) A methyl acrylate, Acrylic-ester (meta); (meta) acrylic acids, such as butyl-acrylate and acrylic-acid (meta) 2-ethylhexyl; A vinyl chloride, (Meta) A halogenation vinyl and halogenation vinylidenes, such as vinyl bromide and a vinylidene chloride; Vinyl acetate, vinyl-esters [, such as a propionic-acid vinyl, ]; (meta) -- nitril [, such as acrylonitrile ]; -- conjugated dienes, such as a butadiene and an isoprene, are mentioned, and even if it carries out the polymerization of these monomers independently, they may carry out copolymerization of the two or more sorts The amount of the vinyl system monomer used has 40 - 60 desirable % of the weight to the whole system.

[0019] As an initiator used for the emulsion polymerization of this invention, although azo system compounds, such as organic peroxide [, such as inorganic peroxides, such as potassium persulfate, an ammonium persulfate, and a hydrogen peroxide, t-butyl peroxide cumene hydroxy peroxide, and PARAMEN tamper oxide, ], azobis diisobutyl nitril, 2, and 2'-azobis (2-amidinopropane) dihydrochloride, are mentioned for example, persulfates, such as potassium persulfate and an ammonium persulfate, are desirable. Moreover, a sodium hydrogensulfite, ferrous-sulfate ammonium, etc. can also be used as a polymerization promotor.

[0020] Although the addition method of a monomer can use a monomer dropping test, a monomer package preparation method, or the pre emulsion method, polymerization stability to its pre emulsion method is desirable. 1 - 5 hours of a maturing time are [ a drop time ] desirable for 1 to 8 hours. Although polymerization temperature is adjusted by the decomposition temperature of an initiator, in the case of a persulfate, 70-80 degrees C is desirable.

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[Translation done.]

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## EXAMPLE

[Example] % in an example is weight % unless it mentions specially.

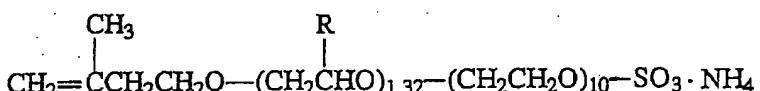
[0022] It blended at a rate which shows the anionic surfactant of the sulfate salt concerning this invention manufactured by the method shown in examples 1-12 and the example 1 of comparison - 3 following, and a conventional type in Table 1, and this invention and the comparative surfactant constituent were prepared. The emulsion polymerization was performed by the method shown below using this surfactant constituent, and the method shown below estimated the performance. A result is shown in Table 1.

[0023] <Example of manufacture of sulfate salt> sulfate salt [A-1] agitator, a thermometer, a tap funnel, and reflux pipe. 3-methyl-3-butene-1-all (made in Tokyo Chemicals) 397g (4.6 mols) and powder sodium METOKI side 3.11g (0.0576 mols) were taught to the reaction container which it had, alpha-olefin epoxide (AOE X24, Daicel Chemical Industries, Ltd. make) 236.7g (1.15 mols) of carbon numbers 12 and 14 was dropped over 4 hours at 130 degrees C under nitrogen-gas-atmosphere mind, and it riped at this temperature for 12 hours. The reflux pipe was changed to the distilling tube and unreacted 3-methyl-3-butene-1-oar was removed under reduced pressure.

According to 1 H-NMR, the number of average addition mols of alpha-olefin epoxide was 1.32. 300g of obtained reaction mixture was taught to the autoclave, and ethyleneoxide 477g was added on condition that 140 degrees C and 0.3MPa. Next, sulfate salt which teaches 87.8g of a part of obtained reaction mixture, and 12.0g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-1] was obtained.

[0024]

[Formula 5]



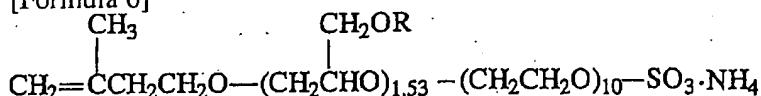
(R : n-C<sub>10</sub>H<sub>21</sub>基とn-C<sub>12</sub>H<sub>25</sub>基の混合物)

[0025] Sulfate salt 3-methyl-3-butene-1-all 310g (3.6 mols) and powder sodium METOKI side 1.95g (0.0361 mols) were taught to the reaction container equipped with [A-2] agitator, the thermometer, the tap funnel, and the reflux pipe, and it was dropped at 130 degrees C under nitrogen-gas-atmosphere mind, having 2-ethylhexyl glycidyl ether 223.6 bet it for 2 hours and a half (1.2 mols), and riped at this temperature for 5 hours. The reflux pipe was changed to the distilling tube and unreacted 3-methyl-3-butene-1-oar was removed under reduced pressure. According to 1 H-NMR, the number of average addition mols of 2-ethylhexyl glycidyl ether was 1.53. 284g of obtained reaction mixture was taught to the autoclave, and ethyleneoxide 438g was added on condition that 130 degrees C and 0.4MPa. Next, sulfate salt which teaches 88.4g of a part of obtained reaction mixture, and 12.6g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed

with the following formula [A-2] was obtained.

[0026]

[Formula 6]

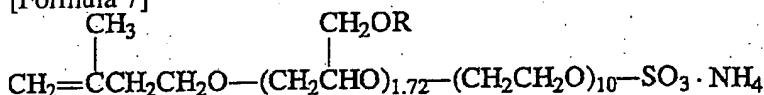


(R : 2-エチルヘキシル基)

[0027] Sulfate salt 3-methyl-3-butene-1-all 1801g (2.1 mols) and powder sodium METOKI side 3.40g (0.0629 mols) were taught to the reaction container equipped with [A-3] agitator, the thermometer, the tap funnel, and the reflux pipe, butyl-glycidyl-ether 273.4g (2.1 mols) was dropped over 2 hours at 140 degrees C under nitrogen-gas-atmosphere mind, and it riped at this temperature for 7 hours. The reflux pipe was changed to the distilling tube and unreacted 3-methyl-3-butene-1-all was removed under reduced pressure. According to 1 H-NMR, the number of average addition mols of butyl glycidyl ether was 1.72. 368g of obtained reaction mixture was taught to the autoclave, and ethyleneoxide 558g was added on condition that 140 degrees C and 0.4MPa. Next, sulfate salt which teaches 82.9g of a part of obtained reaction mixture, and 11.4g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-3] was obtained.

[0028]

[Formula 7]

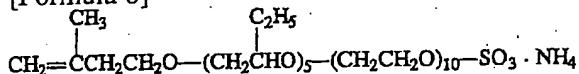


(R : n-C<sub>4</sub>H<sub>9</sub>基)

[0029] Sulfate salt 3-methyl-3-butene-1-all 390g (4.5 mols) and KOH 7.58g (0.1351 mols) were taught to [A-4] autoclave, 1 and 2-epoxy butane 1621g (22.5 mols) was added on condition that 145 degrees C and 0.3MPa, and ethyleneoxide 1985g (45 mols) was continuously added on condition that 150 degrees C and 0.3MPa. Next, sulfate salt which teaches 261g of a part of obtained reaction mixture, and 34.7g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-4] was obtained.

[0030]

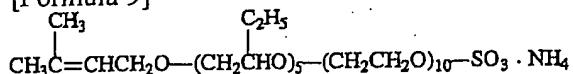
[Formula 8]



[0031] Sulfate salt 3-methyl-2-butene-1-all (made in Tokyo Chemicals) 310g (3.6 mols) and powder sodium METOKI side 7.26g (0.134 mols) were taught to [A-5] autoclave, 1 and 2-epoxy butane 1298g (18 mols) was added on condition that 130 degrees C and 0.3MPa, and ethyleneoxide 1586g (36 mols) was added continuously. Next, sulfate salt which teaches 84.7g of a part of obtained reaction mixture, and 9.60g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfurates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-5] was obtained.

[0032]

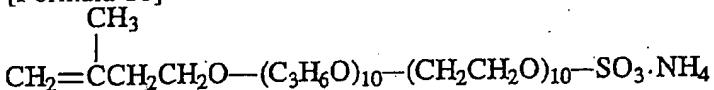
[Formula 9]



[0033] Sulfate salt 3-methyl-3-butene-1-all 301g (3.49 mols) and powder sodium METOKI side 11.3g (0.209 mols) were taught to [A-6] autoclave, propylene oxide 2030g (34.9 mols) was added on condition that 130 degrees C and 0.3MPa, and ethyleneoxide 1537g (34.9 mols) was added continuously. Next, sulfate salt which teaches 81.1g of a part of obtained reaction mixture, and 8.42g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfuates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-6] was obtained.

[0034]

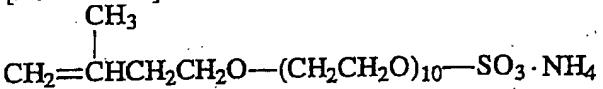
[Formula 10]



[0035] Sulfate salt 3-methyl-3-butene-1-all 340g (3.95 mols) and powder sodium METOKI side 6.40g (0.118 mols) were taught to [A-7] autoclave, and ethyleneoxide 1740g (39.5 mols) was added on condition that 130 degrees C and 0.3MPa. Next, sulfate salt which teaches 100g of a part of obtained reaction mixture, and 19.9g of amidosulfuric acids to the reaction container equipped with the agitator and the thermometer, sulfuates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-7] was obtained.

[0036]

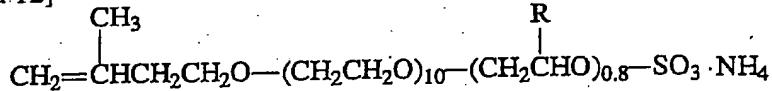
[Formula 11]



[0037] Sulfate salt It is a sulfate salt to the reaction container equipped with [A-8] agitator and the thermometer. 76.7g (0.15 mols) of ten mol adducts of ethyleneoxides of the 3-methyl-3-butene-1-oar obtained by the method shown in the example of manufacture of [A-7], Powder sodium METOKI side 0.243g (0.0045 mols) was taught, alpha-olefin epoxide (AOE X24, Daicel Chemical Industries, Ltd. make) 24.7g (0.12 mols) of carbon numbers 12 and 14 was dropped over 1 hour at 140 degrees C under nitrogen-gas-atmosphere mind, and it riped at this temperature for 4 hours. Next, sulfate salt which adds 14.18g of amidosulfuric acids, sulfuates by making it react for 90 minutes at 120 degrees C under nitrogen-gas-atmosphere mind, removes an unreacted amidosulfuric acid by pressure filtration, and is expressed with the following formula [A-8] was obtained.

[0038]

[Formula 12]



(R : n-C<sub>10</sub>H<sub>21</sub>基とn-C<sub>12</sub>H<sub>25</sub>基の混合物)

[0039] 5.5g of surfactant constituents and 0.28g of potassium persulfate were dissolved in the <emulsion-polymerization method> beaker at 117.8g of \*\*\*\*\* ion exchange water, 2.8g of acrylic acids, 136.1g of butyl acrylates, and 136.1g of methyl methacrylates were added, it emulsified for 5000 r/minx 10 minutes in the homomixer, and the monomer emulsification object was obtained. 137.9g of ion exchange water, 0.25g of potassium persulfate, and the 36.2g of the above-mentioned monomer emulsification objects were taught to the separable flask, and it agitated for 15 minutes in the nitrogen air current. Next, agitating in a nitrogen air current, by the water bath, among flasks, the temperature up was carried out until it became 80 degrees C, the 326.4g of the above-mentioned monomer emulsification objects was dropped over 3 hours after the temperature up from the tap funnel, and after 1-hour digestion, \*\* cooled to the room temperature and obtained the polymer emulsion. The temperature between dropping and digestion and in a flask was kept at 80\*\*2

degrees C. Moreover, when the dropped monomer emulsification object dissociated within a tap funnel, the small agitator was inserted into the tap funnel and homogeneity was maintained.

[0040] The <performance-evaluation method> (1) polymerization stability polymer emulsion was filtered at the wire gauze made from stainless steel of 200 meshes, and the aggregates adhering to a reactor wall, an impeller, etc. after a polymerization were also collected, and it filtered similarly, it carried out 2-hour dryness and weighing capacity at 26.6kPa and 105 degrees C after rinsing, and the amount of aggregates was calculated. Polymerization stability was expressed with weight % of the aggregate to the total amount of the used monomer.

[0041] (2) Polymer emulsion 50g neutralized with 25% aqueous ammonia of mechanical stability was rotated for 5 minutes on condition that 10kgf(s) and 1000 r/min in the chestnut stable tester, the generated aggregate was filtered at the wire gauze made from stainless steel of 200 meshes, and after rinsing a filtration residue, it displayed at 26.6kPa(s) and 105 degrees C by dryness and weight [ as opposed to / carry out weighing capacity and / polymer ] %.

[0042] (3) Dynamic-light-scattering particle-size measuring device coal tar N4 Plus by the mean-particle-diameter Beckmann coal tar company was used, and the mean particle diameter of the polymer emulsion particle neutralized with aqueous ammonia 25% was measured.

[0043] (4) The viscosity Brookfield viscometer was used and the viscosity of the polymer emulsion neutralized with aqueous ammonia 25% was measured by the temperature of 25 degrees C, and rotational frequency 12 r/min.

[0044] (5) The polymer emulsion neutralized with aqueous ammonia 25% was applied on the waterproof slide glass board of a polymer film, it dried at 60 degrees C, and the polymer film was produced. It was under 25-degree C ion exchange water, and the following criteria estimated the milkiness situation.

O after :1-hour progress -- completely -- after milkiness-less O:1-hour progress -- a little -- milkiness  
\*\*:10 - 30 minutes -- milkiness x: -- immediately -- milkiness [0045]

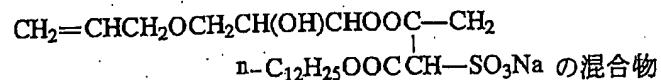
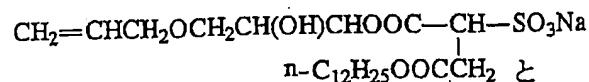
[Table 1].

	界面活性剤組成物(%)		重合 安定性 (%)	機械的 安定性 (%)	平均 粒径 (nm)	粘度 (mPa·s)	ポリマー フィルム の耐水性	
	本発明に係わる 硫酸エステル塩	従来型陰イオン 界面活性剤 <sup>*1</sup>						
実 施 例	1	A-1 (100)	0.15	0.19	178	690	◎	
	2	A-2 (100)	0.28	0.37	152	2060	◎	
	3	A-3 (100)	0.23	0.01	408	37	○	
	4	A-4 (100)	0.22	0.16	244	153	◎	
	5	A-5 (100)	0.17	0.03	371	54	○	
	6	A-6 (100)	0.10	0.01	469	38	○	
	7	A-7 (100)	0.29	0.01	588	1.5	○	
	8	A-8 (100)	0.26	0.01	306	9.3	◎	
	9	A-6 (80) A-1 (20)	0.19	0.11	193	540	◎	
	10	A-7 (80) A-1 (20)	0.17	0.01	281	100	◎	
比 較 例	11	A-6 (80)	B-1 (20)	0.16	0.09	200	453	○
	12	A-6 (20)	B-1 (80)	0.13	0.11	154	2350	○
	1		B-1 (100)	0.62	0.07	164	1518	○
	2		B-2 (100)	0.32	1.2	163	1200	×
	3		B-3 (100)	0.41	0.05	538	5.2	△

[0046] -06. [Formula 13]

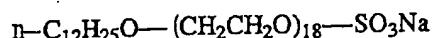
\*1 従来型陰イオン界面活性剤

B-1:

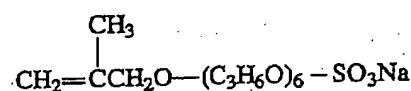


(特開昭58-203960号記載の方法で合成したもの)

B-2:



B-3:



(特開昭61-223011号記載の方法で合成したもの)

[Translation done.]